

## Synthesis and Reactivity Studies of High-Nuclearity Carbido Carbonyl Clusters of Heptarhenium-Iridium and Decaruthenium

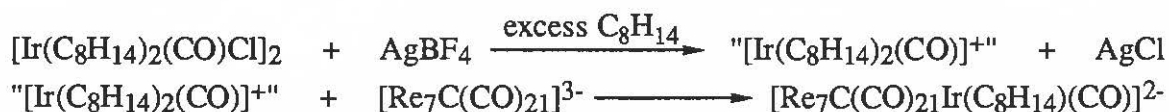
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In the past several years the chemistry of high-nuclearity transition metal clusters has received growing attention [1], owing to its relevance to the understanding of metal-organic substrate interactions on the surfaces of heterogeneous catalysts. The systematic synthesis of these medium-to-large clusters and their reactivities towards small organic molecules are the two major components of current research.

The starting point of our work on the mixed-metal clusters is the preparation and structural characterization of a series of capped heptarhenium carbido carbonyl clusters,  $[\text{Re}_7\text{C}(\text{CO})_{21}\text{ML}_n]^{2-}$ , based on the proposed analogy between the cyclopentadienyl ligand and the cluster trianion  $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$  [2]. In the search for additional examples of this series, we obtained the cluster anion  $[\text{Re}_7\text{C}(\text{CO})_{21}\text{Ir}(\text{C}_8\text{H}_{14})(\text{CO})]^{2-}$  ( $\text{C}_8\text{H}_{14}$  = cyclooctene) via a two step reaction. The  $^{13}\text{C}$  NMR spectrum showed that this anion has a 1,4-bicapped octahedral structure.

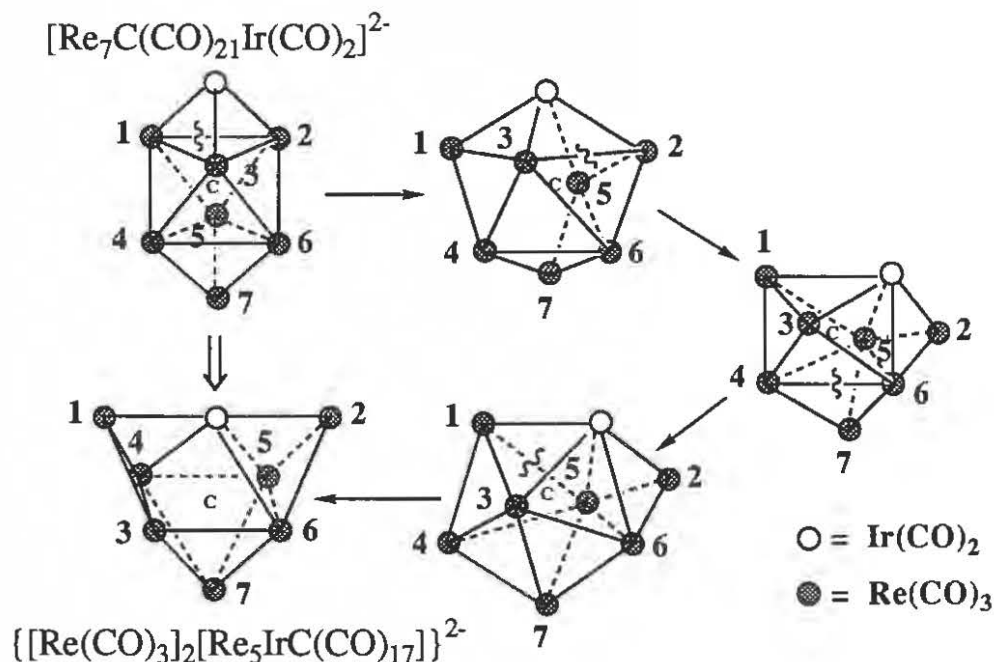


The lability of the cyclooctene ligand in  $[\text{Re}_7\text{C}(\text{CO})_{21}\text{Ir}(\text{C}_8\text{H}_{14})(\text{CO})]^{2-}$  allowed ligand substitution with the formation of  $[\text{Re}_7\text{C}(\text{CO})_{21}\text{Ir}(\text{L})(\text{CO})]^{2-}$  ( $\text{L} = \text{C}_2\text{H}_4, \text{CO}, \text{PPh}_3,$  and  $\text{PMePh}_2$ ). Oxidative addition of triphenylsilane and allyl bromide also occur at iridium, giving  $[\text{Re}_7\text{C}(\text{CO})_{21}\text{Ir}(\text{H})(\text{CO})(\text{SiPh}_3)]^{2-}$  and  $[\text{Re}_7\text{C}(\text{CO})_{21}\text{Ir}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})]^{1-}$  respectively. These derivative compounds were characterized by a combination of IR and NMR spectroscopy, FAB-mass spectrometry, and in selected cases also by X-ray crystallography. During the studies, it was found that the above reactions at the iridium center closely parallel those of an indenyl iridium compound ( $\eta^5\text{-C}_9\text{H}_7$ )  $\text{Ir}(\text{C}_8\text{H}_{14})(\text{CO})$  [3], giving further support for the  $\text{Cp}^- \leftrightarrow [\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$  analogy.

Polyhedral rearrangements are interesting and also intriguing aspects of cluster chemistry [4]. The compound  $[\text{Re}_7\text{C}(\text{CO})_{21}\text{Ir}(\text{CO})_2]^{2-}$  was observed to undergo an irreversible metal framework rearrangement process to give a new isomer  $\{[\text{Re}(\text{CO})_3]_2[\text{Re}_5\text{IrC}(\text{CO})_{17}]\}^{2-}$ , which has a 1,3-bicapped octahedral structure. The isomerization process was found to be a first order reaction with the activation parameters  $\Delta H^\ddagger = 31.0 \pm 0.5$  kcal/mol and  $\Delta S^\ddagger = 13.9 \pm 1.5$  cal/mol·K. A reaction mechanism consisting of multiple diamond-square-diamond processes has been proposed for the framework rearrangement (Scheme I).

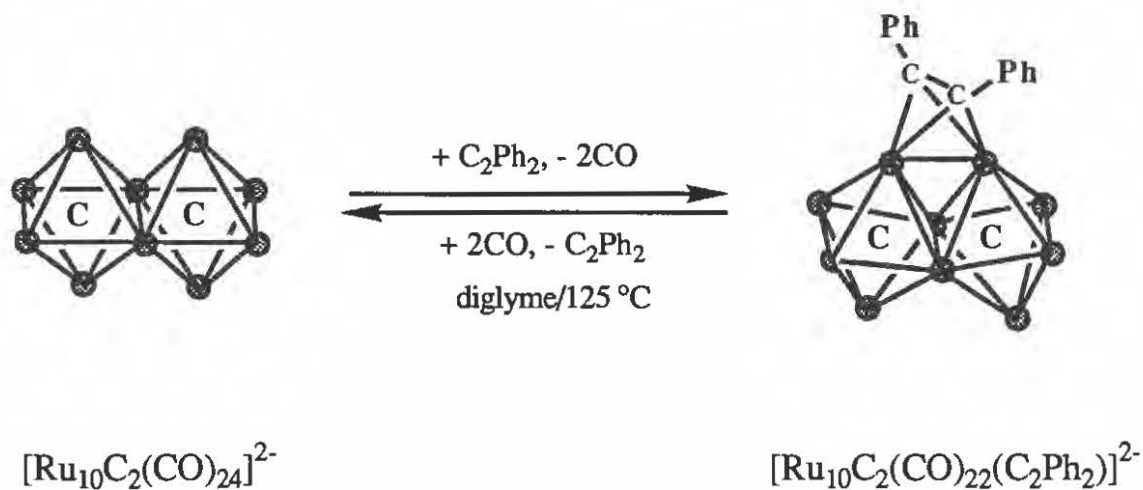
The anion  $\{[\text{Re}(\text{CO})_3]_2[\text{Re}_5\text{IrC}(\text{CO})_{17}]\}^{2-}$  undergoes a decapping reaction in refluxing acetonitrile to give  $[\text{Re}_6\text{IrC}(\text{CO})_{20}]^{3-}$ , which is a structural analog of  $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ . This new trivalent anion also reacts with the transition metal electrophile,  $\text{Au}(\text{PPh}_3)^+$ , giving not only the mono-gold capped compound  $[\text{Re}_6\text{IrC}(\text{CO})_{20}\text{Au}(\text{PPh}_3)]^{2-}$ , but also the di-gold capped cluster  $\{[\text{Re}_6\text{IrC}(\text{CO})_{20}][\text{Au}(\text{PPh}_3)]_2\}^{1-}$ . The structural characterization of both compounds was based on  $^{31}\text{P}$  and variable-temperature  $^{13}\text{C}$  NMR spectroscopy.

Scheme I



The dicarbido-decaruthenium cluster anion  $[\text{Ru}_{10}\text{C}_2(\text{CO})_{24}]^{2-}$  was first prepared by the pyrolysis of  $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$  at 200 - 220 °C in tetraglyme over a period of days [5]. An alternative route, the redox condensation of  $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$  and  $\text{Ru}_5\text{C}(\text{CO})_{15}$ , has been discovered, which represents an improvement by reducing the reaction time and temperature. A diphenylacetylene substituted product,  $[\text{Ru}_{10}\text{C}_2(\text{CO})_{22}(\text{C}_2\text{Ph}_2)]^{2-}$ , has also been synthesized and isolated by column chromatography. An X-ray crystallographic study helped to establish the bonding between the acetylene moiety and the metal core. It was observed that a Ru-Ru bond formed during ligand substitution, and that the acetylene was bound in a  $\mu, \eta^2$  coordination mode (Scheme II).

Scheme II



## References

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